



**CO₂ MINERAL CARBONATION BY OIL SHALE WASTES FROM
ESTONIAN POWER PRODUCTIONS**

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1. Background

CO₂ atmospheric concentration

- **280 ppm** (pre industrialization) → **384 ppm** (2007)
- Annual growth rate **2 ppm** since the year 2000

Meeting the challenge of anthropogenic climate change:

Adaption

Mitigation:

→ **Counter measures:** natural fixation into biomass, dissolution into ocean

→ **Direct reduction:**

→ **Improved efficiency**

→ **Fuel switching:** lower C/H ratio, nuclear power, renewable energy

→ **CO₂ capture and storage:** geological storage, ocean storage,

CO₂ sequestration by mineral carbonation



CO₂ sequestration by mineral carbonation

- Waste residues (from power sector, steel industry and cement industry)

- | | | |
|---|---|--|
| + Usually situated near the CO ₂ emission source | ← | No mining, low transport costs! |
| + Main reactive species are Ca-silicates, CaO,
Ca(OH) ₂ | ← | More reactive towards CO₂! |
| - Limited storage capacity | ← | Not enough for serious
reduction of CO₂ emissions! |

Extra value:

- + **Stabilization of waste material**
- + **By-products with high commercial value (PCC)**



Heat and power production in Estonia is based on combustion of oil shale:

Since 1959 pulverized firing (*PF*).

Since 2004 also the circulating fluidized bed combustion (*CFBC*).

Accompanied by:

1. High CO₂ emissions

+ mineral CO₂ from carbonate decomposition

Total: 948 – 1199 t CO₂/GWh

2. Formation of alkaline ash

~ 5 million tons annually

(Ash content of oil shale is 42 – 48%)



- Ash contains up to **25%** of free **CaO** which strongly basifies (pH 13) transportation waters formed during hydraulic transport of ash.

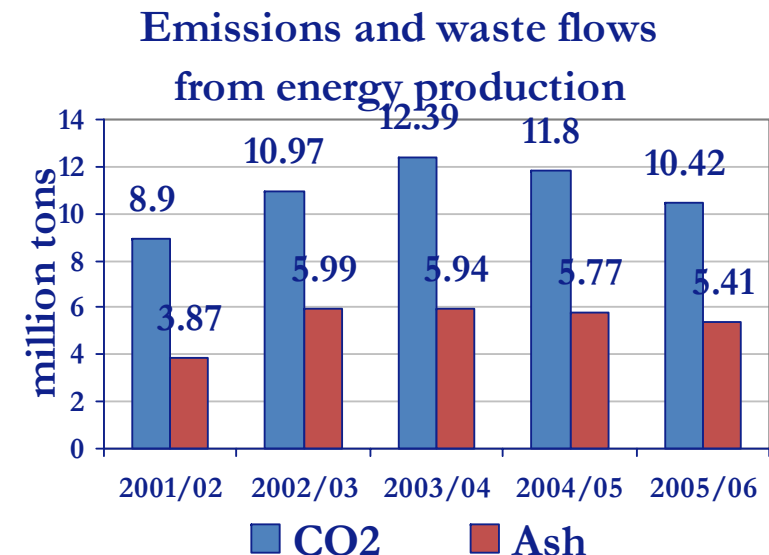
- Ca- and Mg-oxides and silicates could in certain conditions be the binders of CO₂.



Oil shale seam, underground mine, N-E Estonia

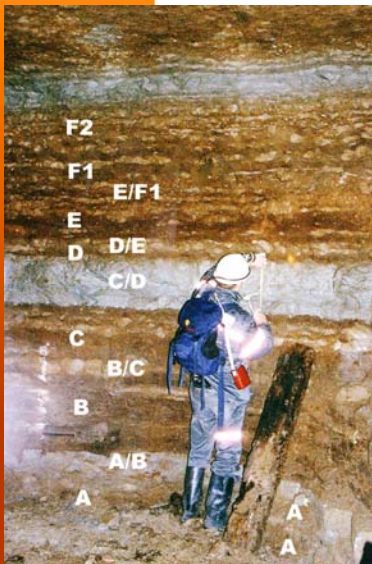


Oil shale opencast, N-E Estonia



Remark:

- Estonian oil shale is a carbonaceous fine-grained sedimentary rock of Ordovician age containing 10–60% kerogen (solid organic matter), 20–70% carbonates represented by limestone, or more rarely by dolomite, and 15–60% siliciclastic minerals.
- During combustion of one tonne of oil shale 450-550 kg of ash is produced (in case of mineral coal only 100 kg of ash is produced).

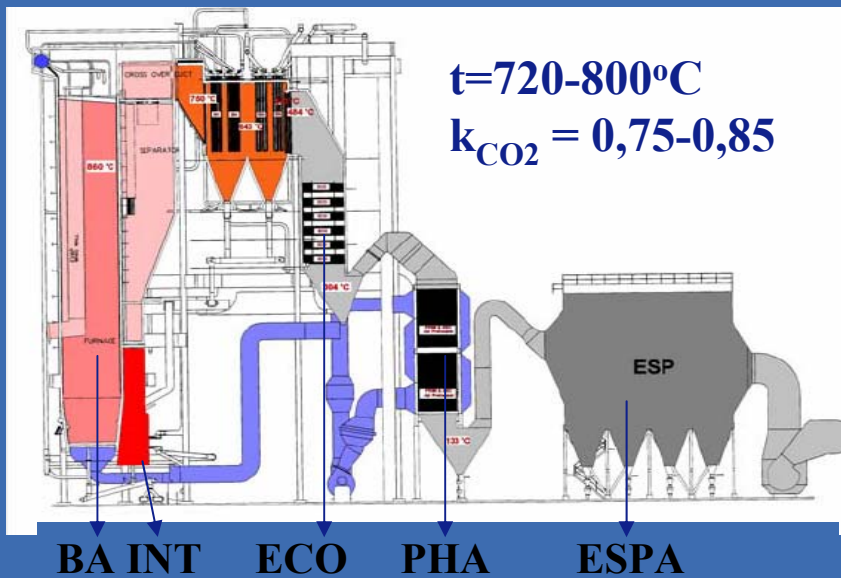


Oil shale seam, underground mine, N-E Estonia



Ash heaps stored in the industrial regions, N-E Estonia

2. Characterization of ashes



Circulated fluidized bed combustion (CFBC)

- BA (bottom ash) ~30%
- INT (Intrex ash) ~11%
- ECO (economizer ash) ~6%
- PHA (air preheater ash) ~3%
- ESPA ~50%

Pulverized firing (PF)

- BA (bottom ash) ~15%
- SHA (superheater ash)
- ECO (economizer ash) } ~15%
- CA (cyclone ash) ~60%
- ESPA (electrostatic precipitator ash)~10%

Phase composition

more lime and
secondary
silicates

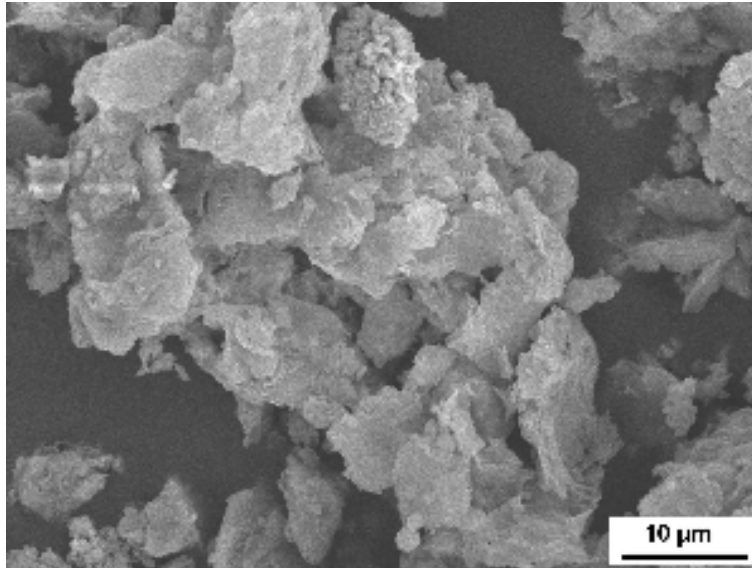
	<u>CFBC ash</u>	<u>PF ash</u>
<u>Lime</u> CaO	3.2-19.9%	14.3-29.3%
<u>Periclase</u> MgO	3.3-7.0%	3.8-7.9%
<u>Melilite</u> $(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	1.0-3.6%	3.2-18.9%
<u>Merwinite</u> $Ca_3Mg(SiO_4)_2$	3.0-5.2%	6.5-13.2%
<u>Belite</u> Ca_2SiO_4	4.6-7.3%	12.3-20.3%
<u>Wollastonite</u> $CaSiO_3$	1.4-3.4%	0.7-2.6%
<u>Orthoclase</u> , $KAlSi_3O_8$	1.3-15.6%	1.7-9.7%
<u>Quarz</u> SiO_2	5.6-17.7%	1.6-10.4%
<u>Calcite</u> $CaCO_3$	4.0-34.8%	2.0-7.6%
<u>Anhydrite</u> $CaSO_4$	8.8-29.9%	4.6-24.1%

more calcite and anhydrite



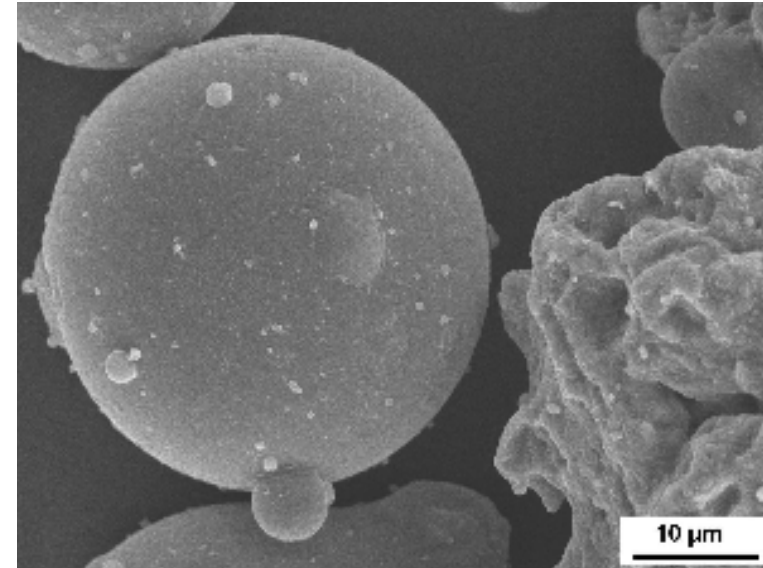
Quantitative XRD performed at Institute of Geology, UT

Morphology



CFBC ash

- Irregular shape;
- Porous and uneven surface;
- The glassy phase is not formed.



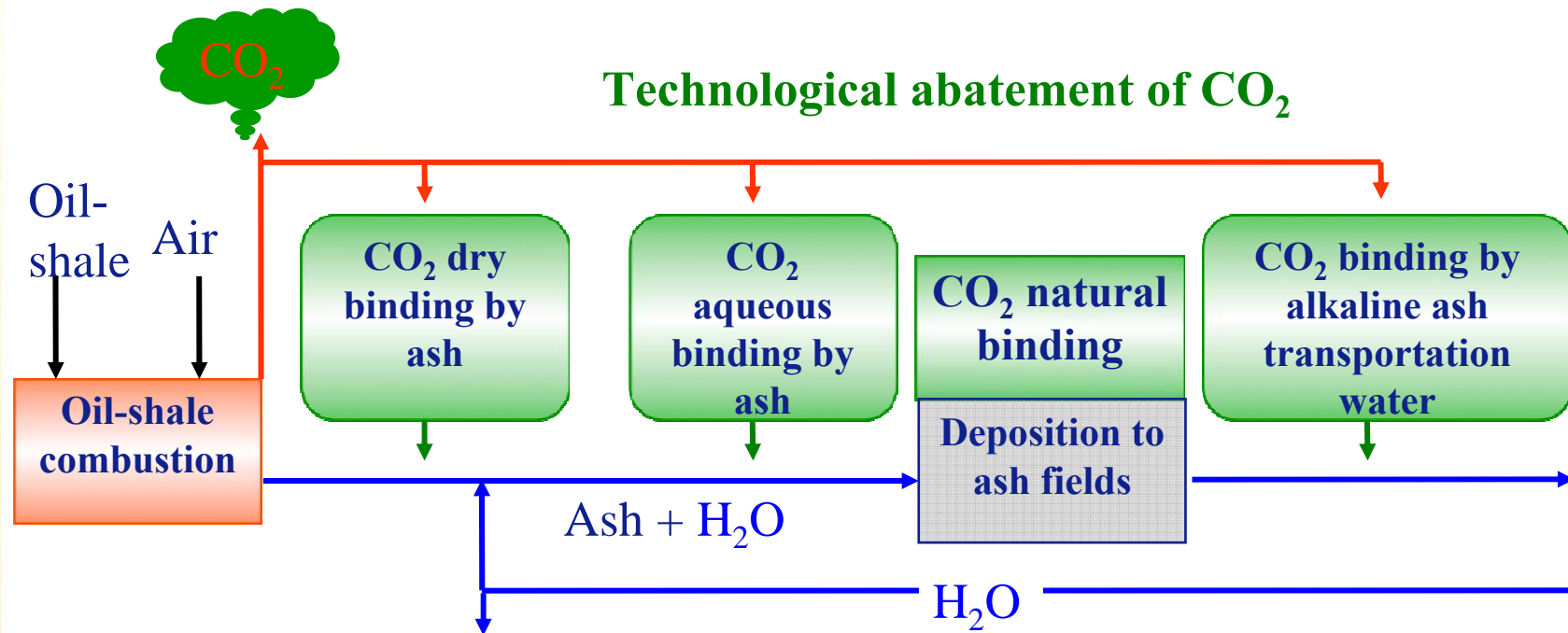
PF ash

- Regular spherical shape;
- Smooth surface;
- The glassy phase is formed.



SEM analysis performed by Dr. V. Mikli at Center of Material Research, TUT

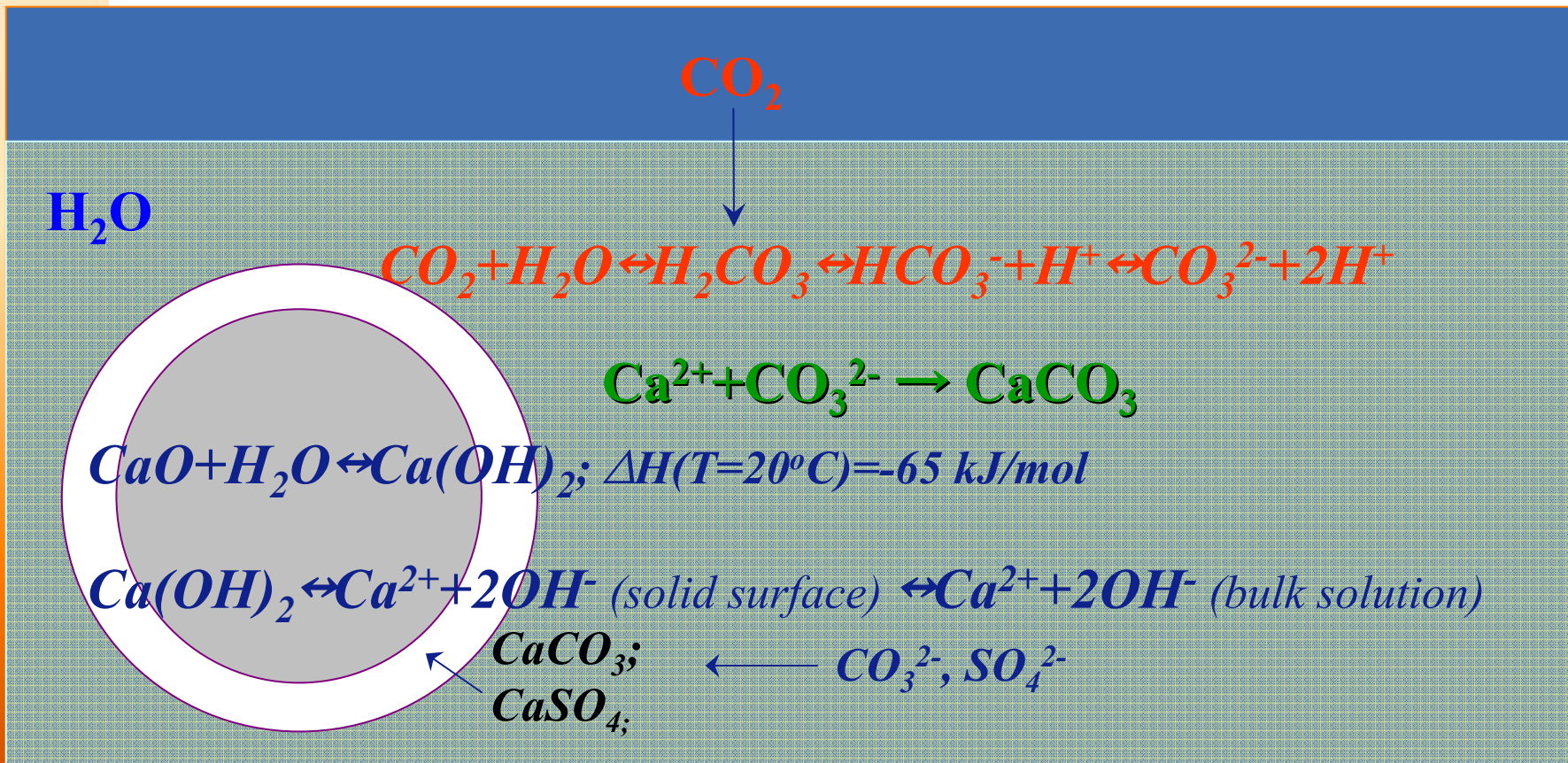
3. Concept of CO₂ mineralization



- The amount of CO₂ emitted during oil shale-based heat and power generation could be diminished by intensification of natural CO₂-binding process occurring during ash transportation and deposition.
- At the same time the alkaline effect of waste ashes is reduced.



4. Reaction Mechanism



In the context of CO_2 sequestration and ash stabilization, **the availability of lime for hydration and carbonation reactions is of key importance.**



- Impact of solution composition
- Impact of specific surface area

Ca-Mg-silicates in aqueous carbonation process

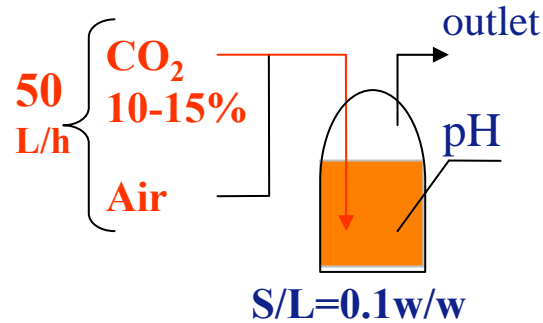


Oil shale ashes contain also Ca-Mg-silicates ($CaSiO_3$, Ca_2SiO_4 , $Ca_3Mg(SiO_4)_2$).
CO₂ dissolves in water to form carbonic acid which dissociates to H⁺ and CO₃²⁻.
The H⁺-ions react with the Ca-(Mg)-silicates, liberating Ca²⁺ (and Mg²⁺)-ions, which in turn react with HCO₃⁻-ions to form solid carbonate.



5. Direct aqueous carbonation of oil shale ash

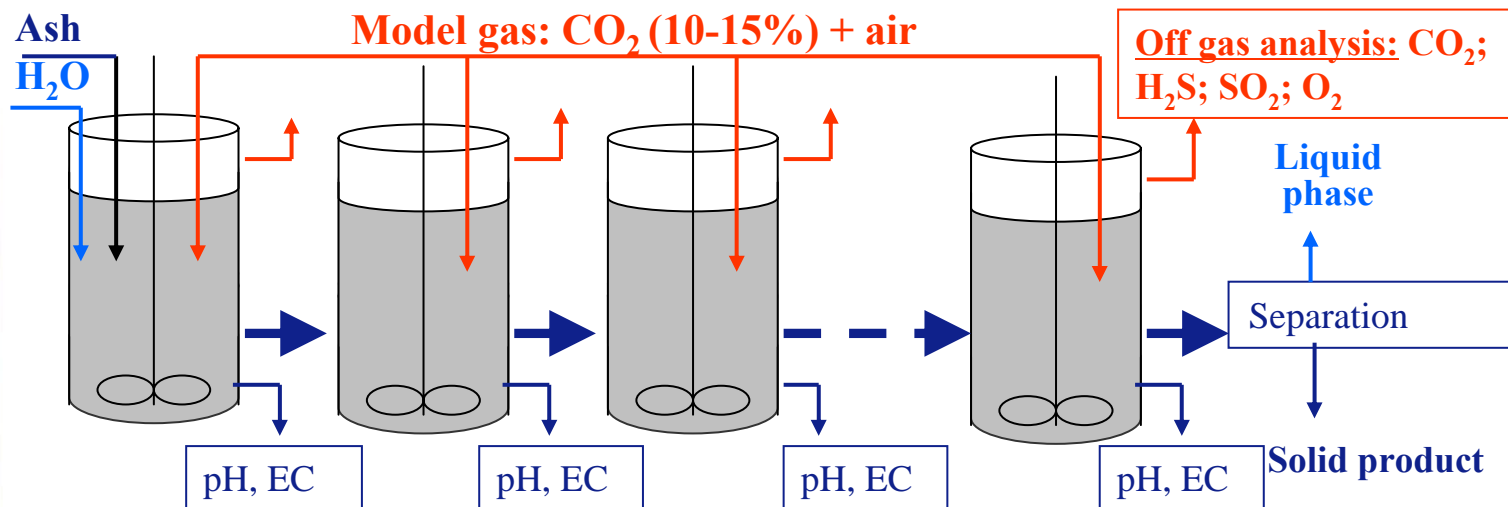
1. Batch process:



Ashes: PF ash $\text{CaO}_f \sim 22.4\%$
 CFBC ash $\text{CaO}_f \sim 12.4\%$

Conditions: $P \sim 1 \text{ atm}$, $t \sim 20^\circ\text{C}$; $S/L = 0.1\text{w/w}$

2. Continuous flow process:



pH=11.5-12

$\text{Ca}^{2+} \sim 1.1-1.5\text{g/L}$

$\text{CaCO}_3 = 18-36\%$

$\text{CaO}_{\text{free}} = 4-15\%$

pH=10-11.5

$\text{Ca}^{2+} \sim 0.8-1.1\text{g/L}$

$\text{CaCO}_3 = 27-43\%$

$\text{CaO}_{\text{free}} = 2-5\%$

pH=7.5-9

$\text{Ca}^{2+} \sim 0.4-0.7\text{g/L}$

$\text{CaCO}_3 = 34-45\%$

$\text{CaO}_{\text{free}} = 0.6-2\%$

pH=6.5-7

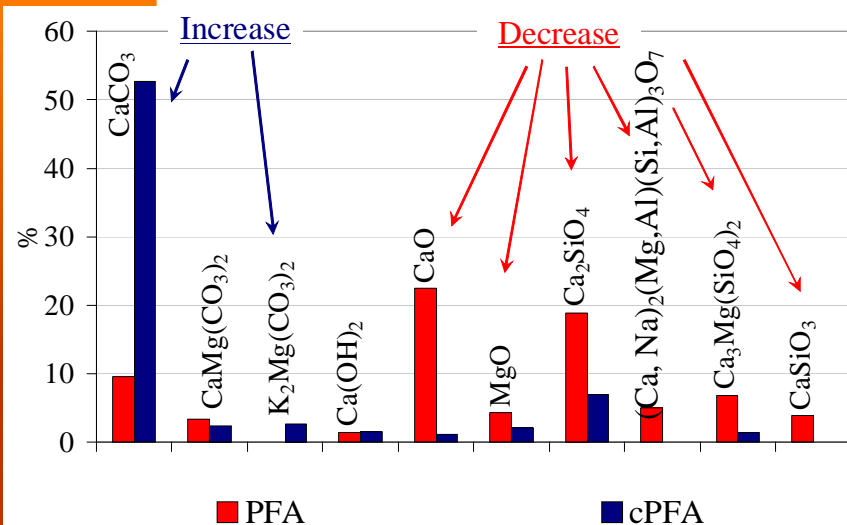
Carbonation of
Ca-Mg-silicates

Direct aqueous carbonation of oil shale ashes

Carbonated ashes	CaO _p , %	CO ₂ , %	BD _{CO₂} , %	CO ₂ ,kg/ash,t (bound)	pH of aqueous solution of solid residue
<u>CFBC ashes</u>	>1	20	87	100	9.0
<u>PF ashes</u>	1-2.9	17-20	65	160	11.0

By extending the carbonation treatment (up to 1 hour) at lower pH region (pH~7) it is possible to increase the amount of CO₂ bound on account of Ca-silicates

(an example based on PF ash):



Total amount of CO₂ bound by PFA
29 g CO₂/100 g PFA

Theoretical CO₂ binding ability:
35 g CO₂/100g PFA

Free CaO

16.15 g CO₂/100 g PFA
CaO, Ca(OH)₂
~56% of the total CO₂ bound

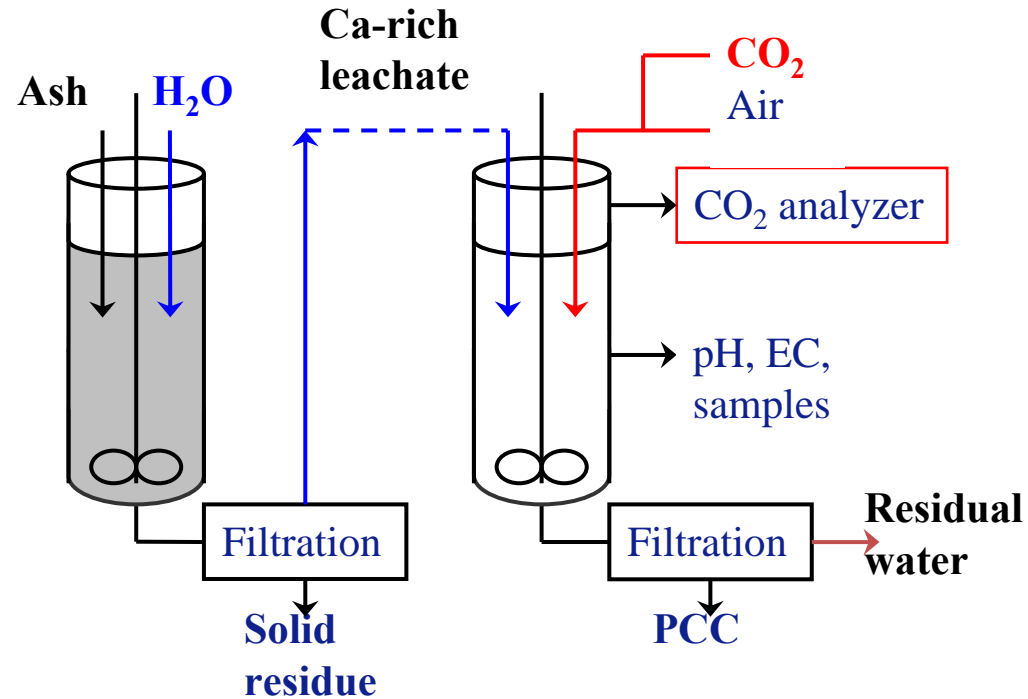
Ca-silicates:

9.61 g CO₂/100g PFA
Predominantly Ca₂SiO₄
~33% of the total CO₂ bound

Other (Mg, K compounds):

3.1 g of CO₂/100g PFA
~11% of the total CO₂ bound

6. Indirect aqueous carbonation of oil shale ash



Step 1.

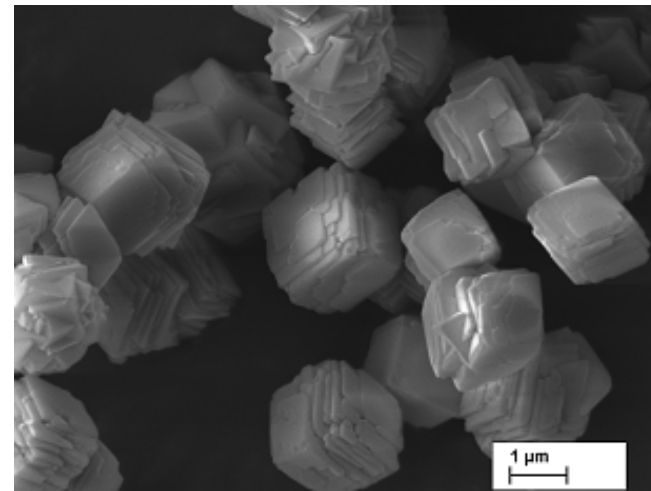
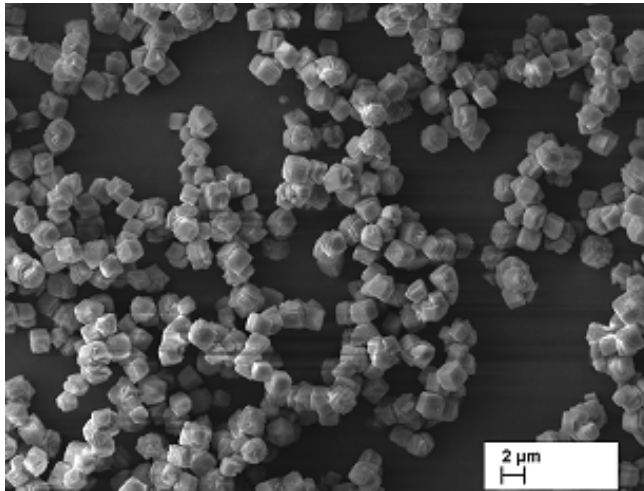
Reactive component (Ca²⁺ion) is extracted from the feedstock (ash).

Step 2.

Reactive component (Ca²⁺ion) is reacted with CO₂ to form solid carbonates.

- $Ca^{2+}(aq) + 2OH^{-}(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$
- $CO_2(g) + OH^{-}(aq) \rightarrow HCO_3^{-}(aq)$

Characterization of solid product (PCC):



$\text{CaCO}_3=94-96\%$

• **Rhombohedral crystal structure**

• **Brightness ISO 2470:1999 93%**

• **Homogeneous particle size distribution ($d_{\text{mean}} = 4-8\mu\text{m}$)**



7. A new method for eliminating CO₂ from flue gases by Ca-containing waste material

The process includes contacting the aqueous suspensions of Ca-containing waste material with CO₂-containing flue gas in two steps:

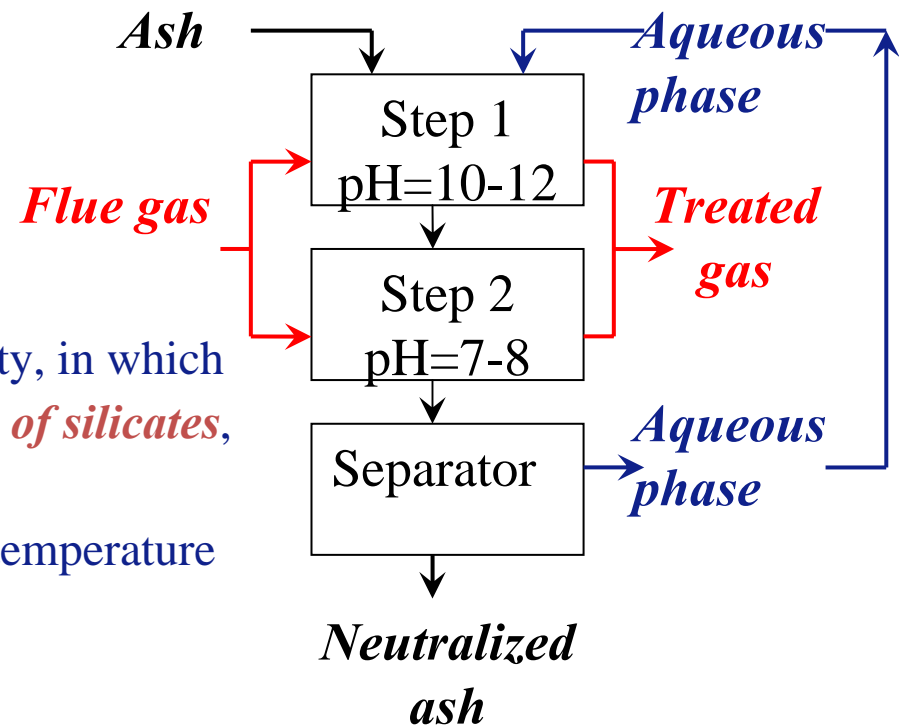
1. **First step:** keeping the pH levels in the range of 10–12.

The water-soluble components such as *free lime* are carbonated in the *first step*.

2. **Second step:** keeping the pH levels in the range of 7–8.

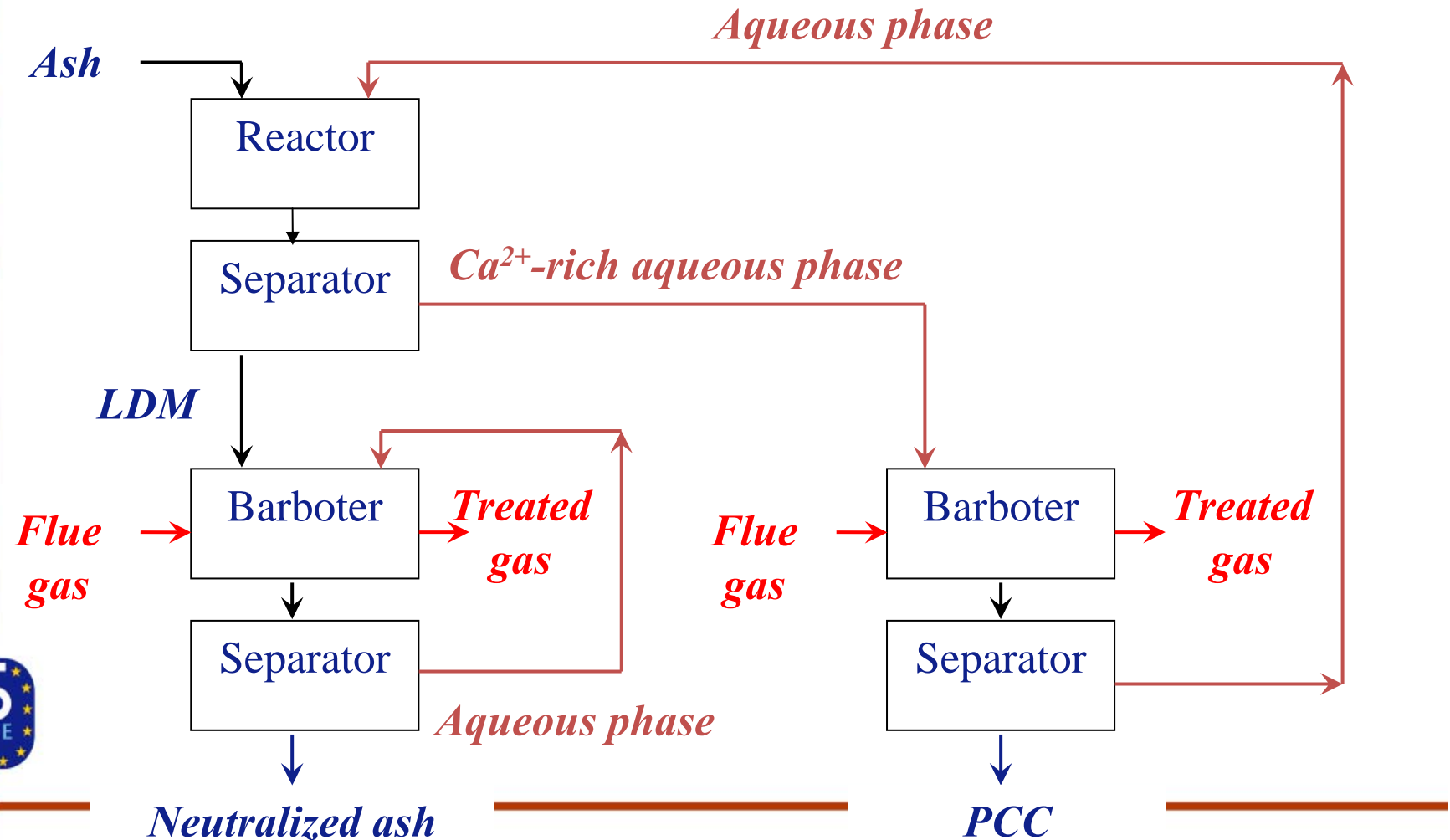
The components of low water-solubility, in which *Ca is generally contained in the form of silicates*, are carbonated in the *second step*.

Conditions: atmospheric pressure, room temperature



As another process route:

1. Separating *free lime* from ash by leaching it into the aqueous solutions in order to produce precipitated calcium carbonate (PCC) as a commercial product.
2. The lime depleted residue (LDM) is able to bind an additional amount of CO₂ on account of *Ca-silicates*.



8. Expected amounts of CO₂ bound

The amount of CO₂ bound per 1 million ton of ash:

1. By ash transportation water 52, 000 t
2. By ash deposits 60,000 t
3. By carbonation of ash suspensions 140,000 t
4. Sum of technological abatement **192,000 t**

10.3% from total CO₂ emitted

62.7% from mineral CO₂ emitted

Per 1 year: 0.9 – 1.0 million t (at production level 2006)

By 1 million m³ of alkaline ash transportation water

- CO₂ captured: **950 - 1000 t**
- PCC formed: **2200 - 2300 t**



9. Conclusions

- The concept of CO₂ mineral sequestration *by* ashes from Estonian power production has been worked out.
- Ashes from oil shale combustion have been characterized as sorbents for CO₂ binding from flue gases in aqueous mineral carbonation processes.
- CO₂ fixation from model gas via direct and indirect aqueous carbonation of oil shale ash at mild operating conditions has been demonstrated:
 - ✓ The CO₂ binding potential of various ash components has been evaluated.
 - ✓ Indirect aqueous carbonation of oil shale ash could provide a waste valorization option by production of precipitated CaCO₃.
 - ✓ Based on multifaceted studies related to carbonation of oil shale ash, a new method for eliminating CO₂ from flue gases by Ca-containing waste material has been proposed.

The total amount of CO₂ bound averaged to **190-210** kg/t ash or 10-11% and 60-65% of the total and mineral carbon content, respectively.



10. Publications of mineral carbonation

by Laboratory of Inorganic Materials, Tallinn University of Technology

- ➔ Kuusik, R., Türn, L., Trikkel, A., Uibu, M., 2002. Carbon dioxide binding in the heterogeneous systems formed at combustion of oil shale. 2. Interactions of system components - thermodynamic analysis. Oil Shale 19, 143-160.
- ➔ Kuusik, R., Uibu, M., Kirsimäe, K., 2005. Characterization of oil shale ashes formed at industrial scale boilers. Oil Shale 22, 407-420.
- ➔ Kuusik, R., Uibu, M., Toom, M., Muulmann, M.-L., Kaljuvee, T., Trikkel, A., 2005. Sulphation and carbonization of oil shale CFBC ashes in heterogeneous systems. Oil Shale 22, 421-434.
- ➔ Kuusik, R., Uibu, M., Uus, M., Velts, O., Trikkel, A., Veinjärv, R., 2009. Method for eliminating CO₂ from flue gases by calcium compounds containing industrial wastes. Estonia.
- ➔ Kuusik, R., Uus, M., Uibu, M., Stroganov, G., Parts, O., Trikkel, A., Pepoyan, V., Terentiev, A., Kalnapenk, E., 2006. Method for neutralization of alkaline waste water with carbon dioxide consisting in flue gas.
- ➔ Uibu, M., Uus, M., Kuusik, R., 2009. CO₂ mineral sequestration in oil shale wastes from Estonian power production. Journal of Environmental Management 90, 1253-1260.
- ➔ Uibu, M., Velts, O., Kuusik, R., 2010. Developments in CO₂ mineral carbonation of oil shale ash. Journal of Hazardous Materials 174, 209-214.
- ➔ Velts, O., Hautaniemi, M., Kallas, J., Kuosa, M., Kuusik, R., 2010. Modeling calcium dissolution from oil shale ash: Part 2. Continuous washing of the ash layer. Fuel Processing Technology 91, 491–495.
- ➔ Velts, O., Hautaniemi, M., Kallas, J., Kuusik, R., 2010. Modeling calcium dissolution from oil shale ash: Part 1. Ca dissolution during ash washing in a batch reactor. Fuel Processing Technology 91, 486–490.



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Thank You very much!



Remark 2:

→ About 77% of the mined oil shale with lower calorific value is used as boiler fuel in large power plants. During combustion of oil shale CO₂ is formed not only as a burning product of organic carbon, but also as a decomposition product of the ash carbonate part. Therefore the total content of carbon dioxide increases up to 15% in flue gases of oil-shale. Oil shale ash contains up to 20-25% free Ca-Mg oxides. Portlandite Ca(OH)₂ forming from free lime during hydraulic transportation and wet deposition of ash can bind CO₂ also from air. Natural weathering process could be accelerated by simple methods. It has been demonstrated by batch and continuous mode experiments, that by processing of the ash – water suspension by flue gases, the CO₂ binding ability of ash could be utilized completely. The results of these experiments show that watered oil shale ash can bind 80-160 kg and more of CO₂ per one tonne of ash, and 30-80 kg CO₂ could be bound by alkaline wastewater used for transportation of one tonne of ash [6]. From annual production of about **16.3 mln tonnes of oil shale in Estonia in 2007, 14.3 mln t (88%)** are the share of oil shale combustion by Energy Sector. Taking into account that 450-550 kg of ash is produced from every one tonne of combusted oil shale, about **7 mln tonnes of ash was produced in 2007**. The amount of CO₂ bound by oil shale ash in wet mineralization process by flue gas could reach 560 – 1120 thousand tonnes and by alkaline wastewater neutralization process in reactor 210– 560 thousand tonnes. The maximum amount of CO₂ bound with flue gas could be summarized as 770 – 1680 thousand tonnes. Taking into account that big industrial Energy enterprises using mainly oil shale produced 14.5 million tonnes CO₂ in 2007, the CO₂ amount which is possible to bind with oil shale ash and transportation water by flue gas could reach 10-12% of emitted by power plants CO₂ [6, 7]. There exist some prerequisites that carbonates formed as result of the binding process could be separated and used as independent by-product, but more useful is to store them in the closed oil-shale mines. The last solution will permit to fill underground mining cavities and to prevent environmental problems arising from ash heaps.

